Advanced Water Gas Shift Membrane Reactor
(DE-FC26-05NT42453)

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16 May 2006

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2) QuesTek Innovations, Evanston, IL
3) Metal Hydride Technologies Inc., Burlington, VT

Project ID: PDP 26

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Overview

Timeline

- Start – July 2005
- End – June 2007
- 46% Complete

Budget

- Total Project Funding
  - DOE share - $849k
  - Contractor share - $212k
- Funding Received in FY05
  - $305k
- Funding for FY06
  - $308k

Barriers

- Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan
  - Section 3.1.4.2.3: Separations and Other Cross-Cutting Hydrogen Production Barriers (DOE Office of Energy Efficiency and Renewable Energy)
  - M. Impurities
- Hydrogen from Coal – Research, Development, and Demonstration Plan
  - Section 5.1.5 Technical Barriers – Central Production Pathway (DOE Office of Fossil Energy)
  - D. Impurity Intolerance/Catalyst Durability
  - I. Poisoning of Catalytic Surfaces
  - Q. Impurities in Hydrogen from Coal

Partners

- QuesTek Innovations LLC
- Metal Hydride Technologies

Objectives

- **Overall**
  - Identify through Atomistic and Thermodynamic modeling a suitable Pd-Cu tri-metallic alloy membrane with high stability and commercially relevant hydrogen permeation in the presence of carbon monoxide and trace amounts of sulfur.
  - Identify and synthesize a Water Gas Shift (WGS) catalyst with a high operating life that is sulfur and chlorine tolerant at low concentrations (0.004 atm Partial Pressure) of these impurities.
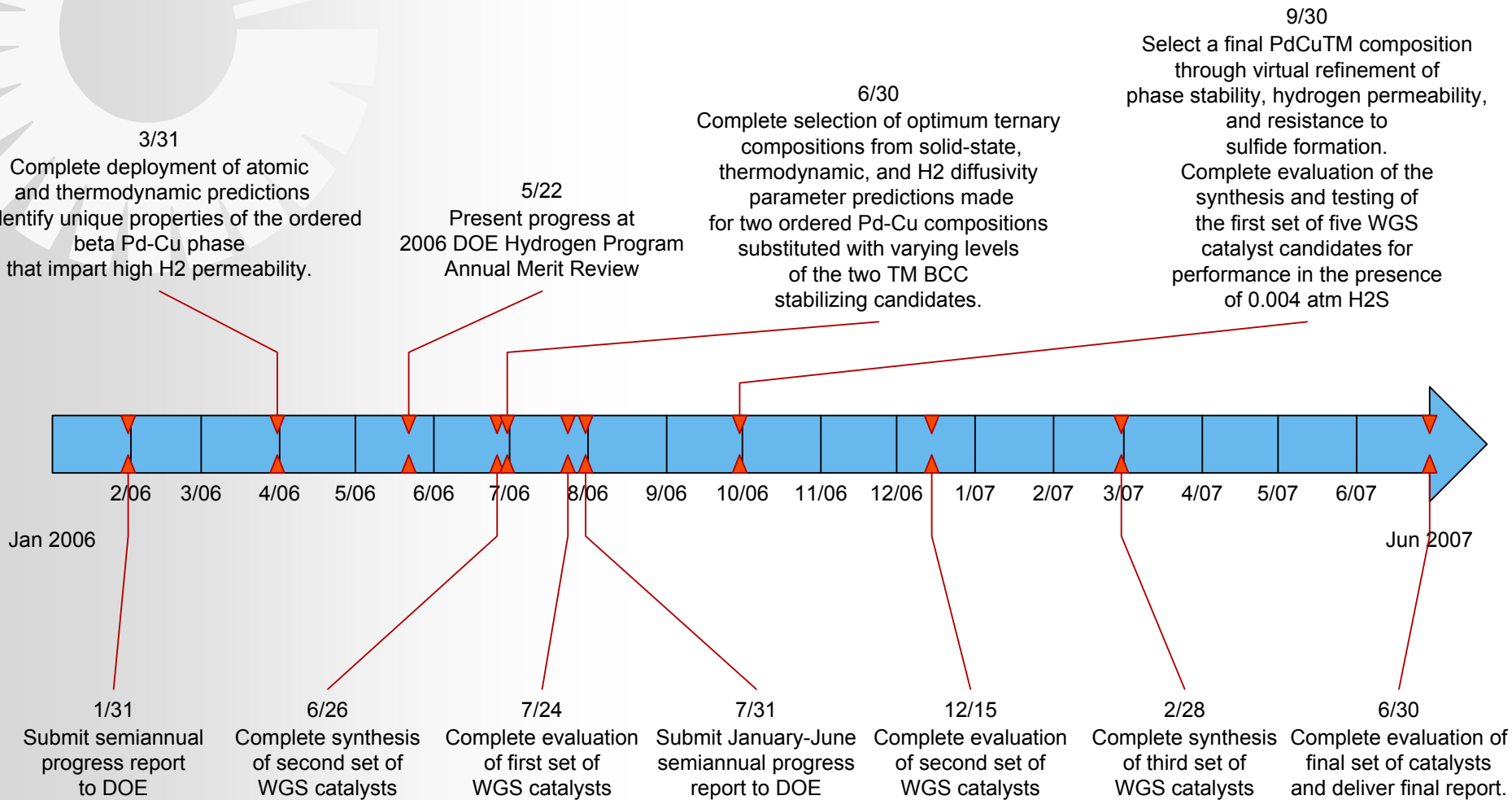
- **FY2006**
  - (Oct-Dec 2005) Complete screening and down-select from six to two Transition Metal (TM) substituents for PdCuTM alloy candidates demonstrating best potential to enhance stability of the ordered, beta (BCC) PdCu phase over an extended alloy composition and temperature range.
  - (Jan-Mar 2006) Complete deployment of atomic and thermodynamic predictions to identify the unique properties of the ordered beta (BCC) Pd-Cu phase that impart high H_2 permeability.
  - (Apr-Jun 2006) Complete selection of optimum ternary compositions from solid-state, thermodynamic, and H_2 diffusivity parameter predictions made for two ordered Pd-Cu compositions substituted with varying levels of the two TM BCC stabilizing candidates.
  - (Jul-Sep 2006) Select a final PdCuTM composition through virtual refinement of phase stability, hydrogen permeability, and resistance to sulfide formation. Complete evaluation of the synthesis and testing of the first set of five WGS catalyst candidates for performance in the presence of 0.004 atm H_2S.

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Combine Hydrogen Separation with ~43 Atm. Water Gas Shift ($H_2O + CO \Leftrightarrow H_2 + CO_2$) in Presence of H_2S & COS

- Some Pd-Cu alloys reportedly have sulfur tolerance and the BCC Pd-Cu phase has high H permeance but lower thermal stability and questionable chemical stability in the presence of Sulfur and Cox than the FCC phase.

- **Approach:** Use VASP atomistic modeling and thermodynamic parameter estimation to predict higher stability BCC Pd-Cu based trimetallic alloys with commercial relevant permeance.

- Pt-Re/Doped Ceria-Zirconia and Pt-Re/Titania based catalysts have been reported to have acceptable volumetric Water Gas Shift Activity at ~ 1 Atm and ~ 2 ppmv H_2S with natural gas or diesel reformate.

- **Approach:** Combine: 1) Prepare high surface area, low mass transfer resistance, very high dispersion Pt base mixed metal cluster catalysts on doped nano-engineered oxides. 2) Chose dopants that are likely to increase sulfur tolerance using VASP atomistic modeling. 3) Validate modeling approach through kinetic evaluation with and without sulfur and after aging in 0.004 atm H_2S reformate. Down select to final composition.

Plan and Time Line

3/31
Complete deployment of atomic and thermodynamic predictions to identify unique properties of the ordered beta Pd-Cu phase that impart high H2 permeability.

5/22
Present progress at 2006 DOE Hydrogen Program Annual Merit Review

6/30
Complete selection of optimum ternary compositions from solid-state, thermodynamic, and H2 diffusivity parameter predictions made for two ordered Pd-Cu compositions substituted with varying levels of the two TM BCC stabilizing candidates.

9/30
Select a final PdCuTM composition through virtual refinement of phase stability, hydrogen permeability, and resistance to sulfide formation. Complete evaluation of the synthesis and testing of the first set of five WGS catalyst candidates for performance in the presence of 0.004 atm H2S

2/06   3/06   4/06   5/06   6/06   7/06   8/06   9/06   10/06   11/06   12/06   1/07   2/07   3/07   4/07   5/07   6/07

Jan 2006

Jun 2007

1/31
Submit semiannual progress report to DOE

6/26
Complete synthesis of second set of WGS catalysts

7/24
Complete evaluation of first set of WGS catalysts

7/31
Submit January-June semiannual progress report to DOE

12/15
Complete evaluation of second set of WGS catalysts

2/28
Complete synthesis of third set of WGS catalysts

6/30
Complete evaluation of final set of catalysts and deliver final report.

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Critical Assumptions and Issues

Assumptions

- Atomistic & Thermodynamic Modeling will be a reliable guide to new Sulfur Tolerant, thermally stable membrane with commercial relevant hydrogen permeance.
- High H_2O to H_2S Partial Pressure will mitigate support sulfidation and oxy-sulfidation
- Dopants can mitigate oxide over-reduction at high H_2 and CO partial pressures
    - Preventing over reduction should prevent excessive surface carbonate formation
- In the Pt-Re/CeZrOx case, the Gorte mechanism is the dominant WGS route

Issues

- Achieving stable, equal flow operation across all 5 reactors under target conditions at ~ 43 atm total pressure with high steam to CO ratio proved to be very difficult.
    - Initial calibrated orifice design unreliable
    - New larger diameter steam generator and other modifications being implemented
    - 2nd set of catalysts will be tested under target conditions.

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Outline of Technical Progress

- Atomistic and Thermodynamic Modeling of potential trimetallic BCC phase PdCuTm alloys
    - Down selection of two leading candidates
    - Benchmarking B2 phase PdCuH system
- Atomistic modeling of potential dopants for the TiO_2 based catalyst system.
- Identification and some physical characterization of first set of 5 Pt-Re Oxide catalysts
- Initial sulfur free catalyst performance results

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New Thermodynamic Model for Pd-Cu Binary System

First step to a viable model for BCC phase trimetallic Pd-Cu-TM w & w-o H$_2$
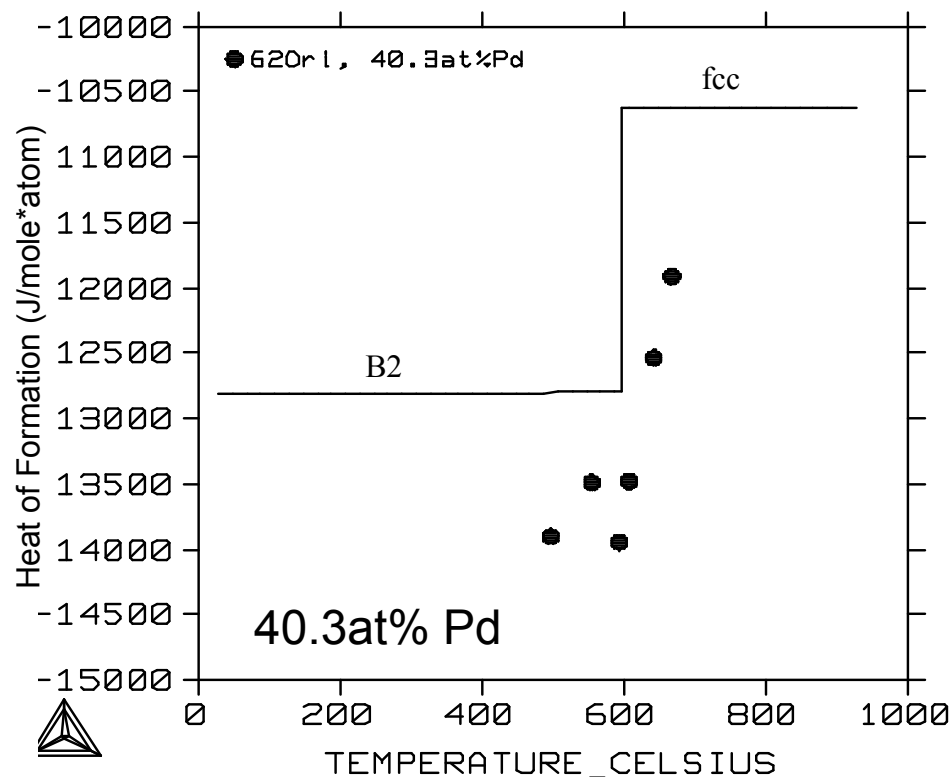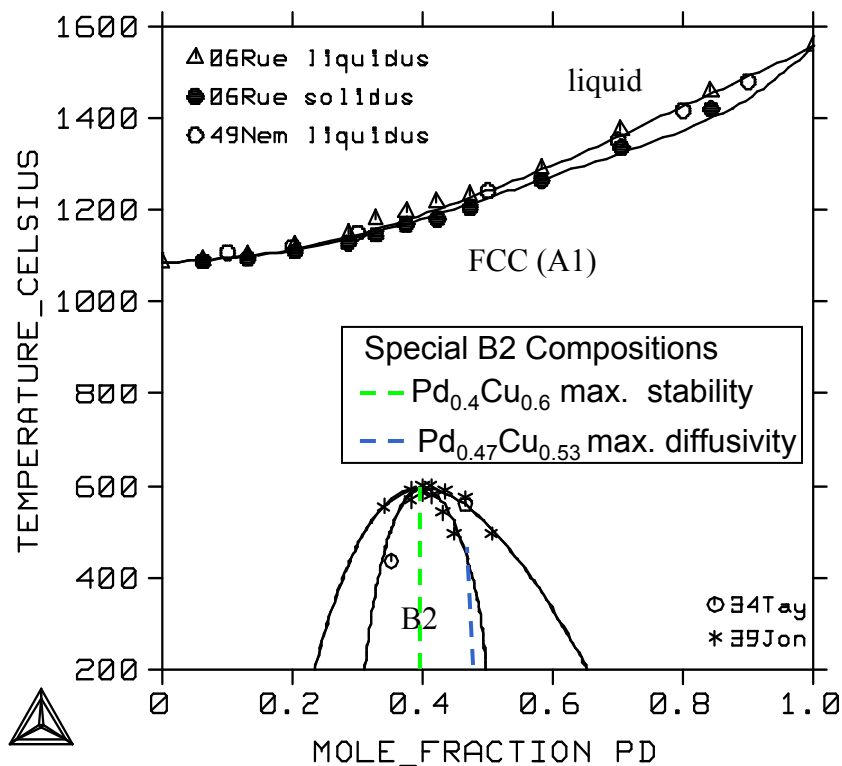
A complete Cu-Pd thermodynamic description including the ordered B2 phase.

Thermodynamic & First-Principles Modeling Comparison

VASP minimized structures using PAW GGA PW hard potentials:
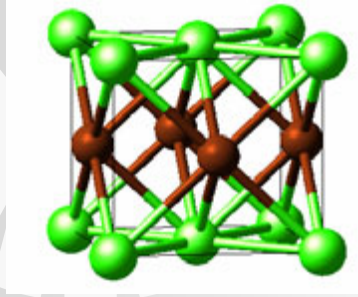
$Pd_{0.5}Cu_{0.5}$ ordered FCC
a=3.805 Å
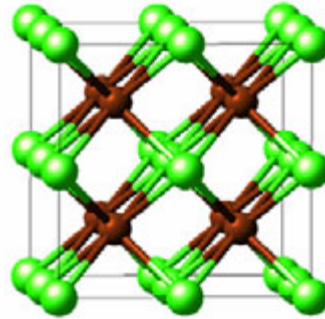
$Pd_{0.5}Cu_{0.5}$ B2 2x2x2
a=3.013 Å
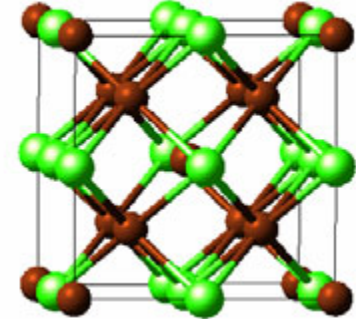
$Pd_{0.4}Cu_{0.6}$ B2 2x2x2
a=2.982 Å

Comparison of MedeA Phonon direct method thermodynamic predictions (○) with thermodynamic modeling of experimental data (———):

$Pd_{0.5}Cu_{0.5}$ FCC Ordered

$Pd_{0.5}Cu_{0.5}$ BCC Ordered

$Pd_{0.4}Cu_{0.6}$ BCC Ordered
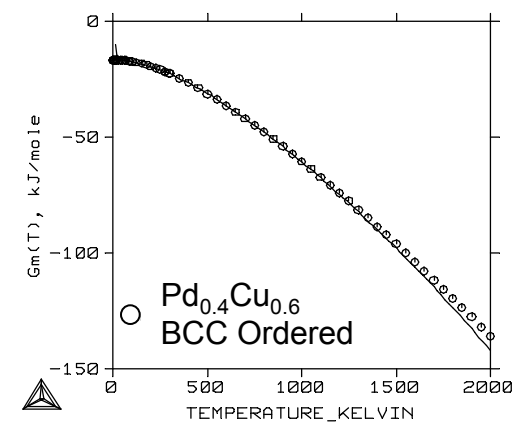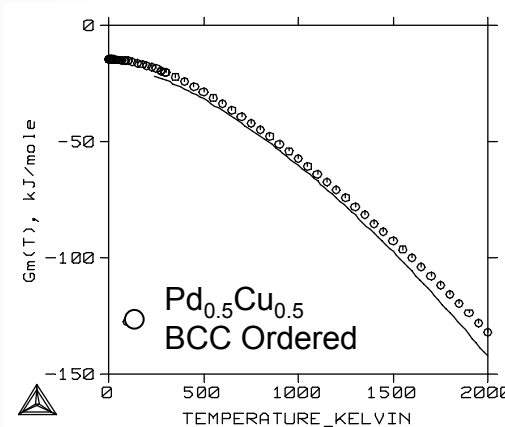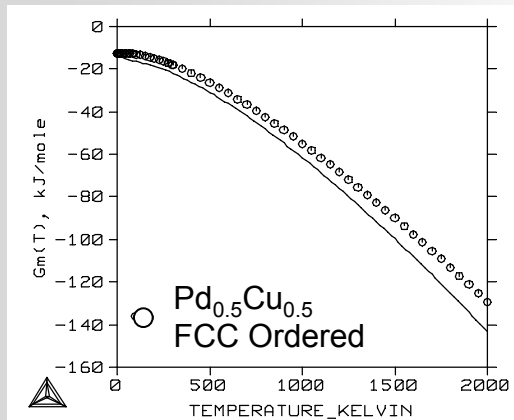
Excellent agreement serves to validate first-principles thermodynamic predictions. High stability of $Pd_{0.4}Cu_{0.6}$ ordered B2 phase confirmed.

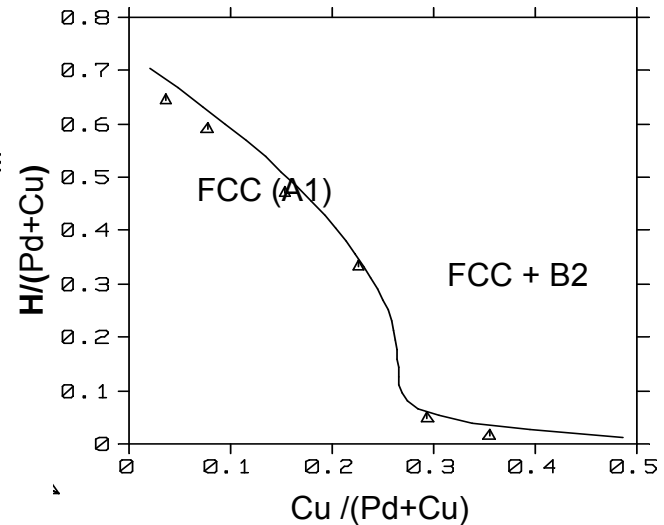# New H Solubility In PdCu B2 Phase Data Incorporated Into Thermodynamic Model

——————— Thermodynamic Model

B2 Phase Pd-Cu composition narrows with increasing H content

Experimental Data

03Fla,303K
△ 0%Cu
■ 5%Cu
◆ 9.6%Cu
⬣ 15%Cu
▼ 20%Cu
▲ 30%Cu
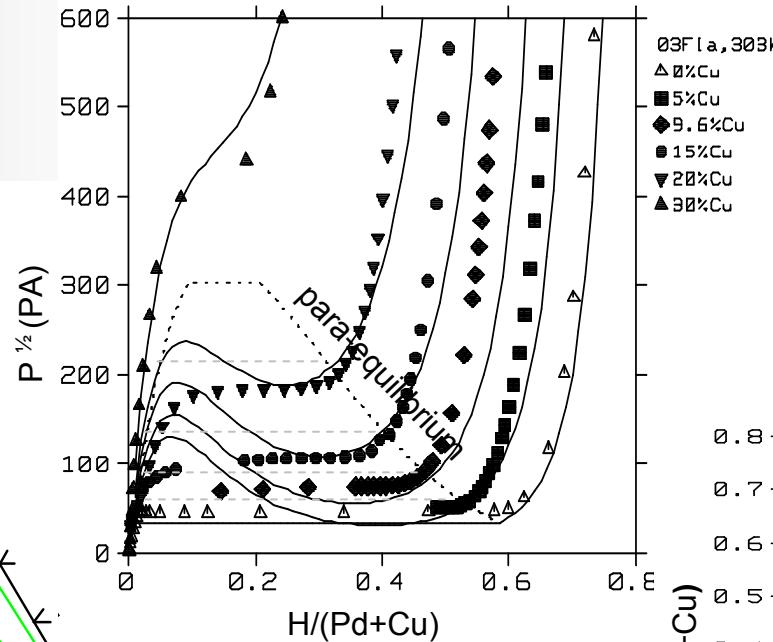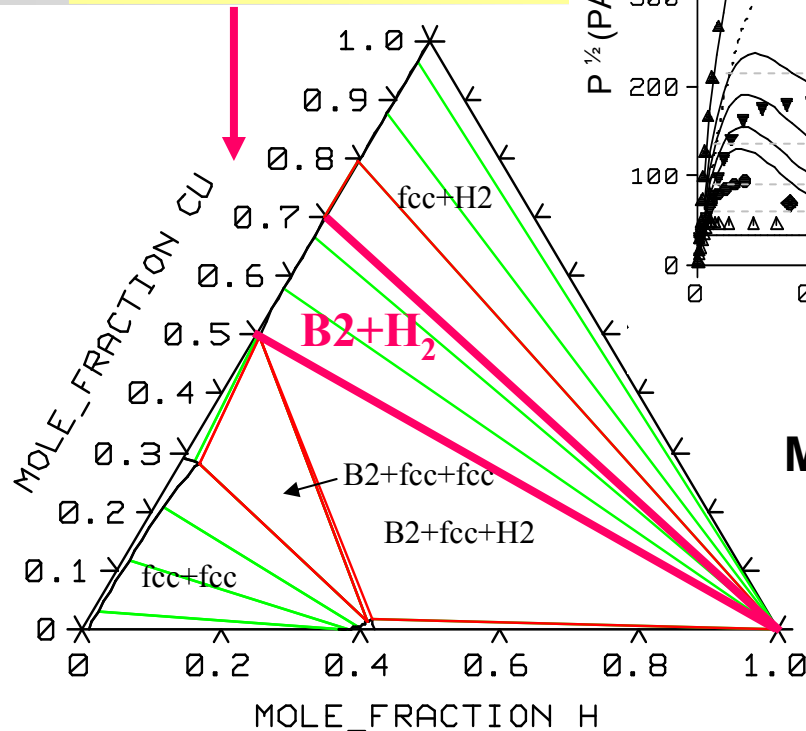
FCC-FCC Miscibility Gap

Pd-Cu-H Section T= 303 K P=10^5 Pa

H Solubility in CuPd alloys

T= 298 K P=10^5 Pa

Combined First-Principles, Experimental, and Thermodynamic Investigations of H in PdCu B2

Observation & prediction agreement increases confidence in PdCuTm H work

0.06 Mole-Fraction H in Pd0.5Cu0.5 Ordered B2		
Full Ground State Minimization		
H Interstitial Site	ΔV	$\Delta H_{form\ elect}$ (0K)
	(cm^3/MoleH)	(kJ/Mole*atom)
Alpha-Octahedral	0.12	-8.64
Beta-Octahedral	0.10	-9.28
Tetrahedral	0.12	-9.43

Diffusion Coefficent Comparison	D (m^2/s)
Phase / Source	at 57 C/ 330 K
BCC Pd$_{0.50}$Cu$_{0.50}$ Prediction (UTRC)	2.20E-09
BCC Pd$_{0.47}$Cu$_{0.53}$ Experiment (Völkl, 1978)	5.73E-09
FCC Pd$_{0.47}$Cu$_{0.53}$ Experiment (Völkl, 1978)	1.80E-12

J. Völkl, G. Alefeld, in *Hydrogen in Metals*, Vol. I, G. Alefeld, J. Völkl, Eds., Berlin: Springer Verlag, (1978).

- ○ VASP first-principles predictions
- □ H solubility measurements
- — Thermodynamic modeling

Pd0.44Cu0.56

Pd0.50Cu0.50

Tangent for H partial enthalpy
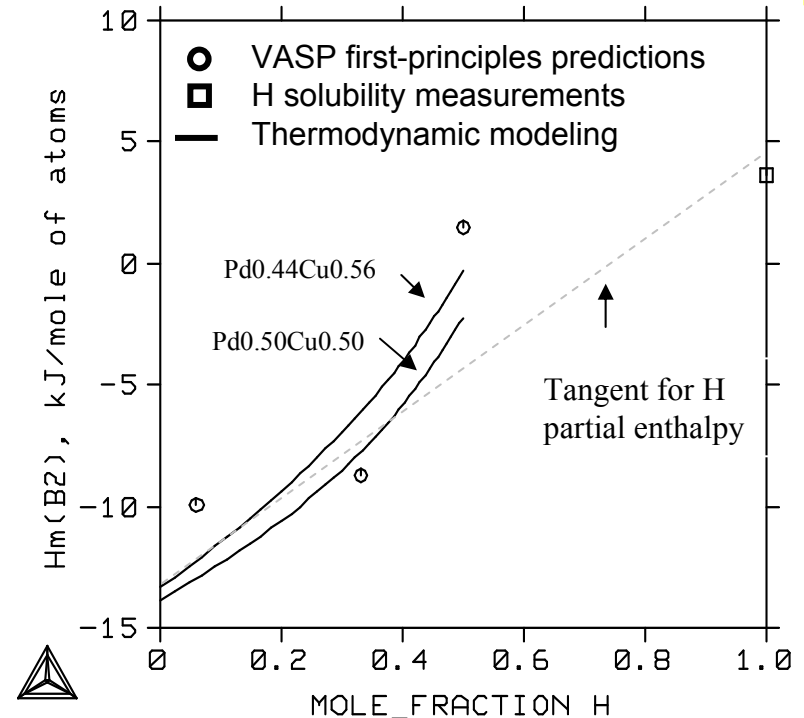
The enthalpy of formation at 298°K, relative to pure element at 298°K (fcc-Cu, fcc-Pd, gas-H2). The calculated partial H(H) is 4.45 kJ/mole H, experimental 3.6 kJ.

H solubility and diffusivity parameters benchmarked in PdCu B2 system.

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Transition Metal (TM) Substitution in $Pd_{0.5}Cu_{0.5}$ B2

Composition	$\Delta H_{sub\ elect}(0\ K)$ (kJ/mole*atom)	ΔVolume ($Å^3$/atom)
Pd_8Cu_8	-	-
Pd_8Cu_7(R4)	2.17	-0.01
Pd_7(T5)Cu_8	0.84	0.14
Pd_8Cu_7(G5)	-7.12	0.42
Pd_8Cu_7(J5)	2.39	0.29
Pd_8Cu_7(G6)	-9.67	0.42
Pd_8Cu_7(J6)	1.64	0.29
Pd_8Cu_7(G4)	-4.17	0.10

VASP: PAW GGA PW hard potentials

TM = R4, T5, G4, G5, G6

$$\Delta H_{sub\ elect}\ (0\ K) = E(0\ K)_{composition} - (E(0\ K)_{Pd8Cu8} + E(0K)_{TM})$$

TM substituted in $Pd8Cu8$ 2x2x2
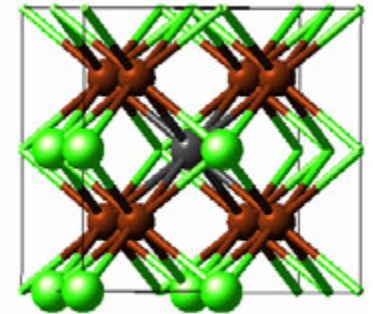
Pd_7TMCu_8 TM substituted for Pd
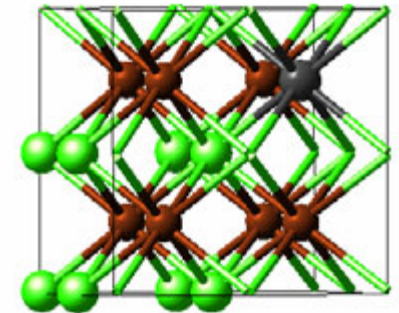
Pd_8Cu_7TM TM substituted for Cu

Substitution of most TM more favorable on Cu sublattice . Some TM have both favorable, exothermic heats of substitution and increased volume.

2

TM Substitution Influence on $Pd_{0.5}Cu_{0.5}$ B2 (110) Slab

Sub-surface sites favored by most TM substituents

Composition 110 2x2x2 Slab	$\Delta H_{form\ elect}$ (0 K) (kJ/mole*atom)	Surface Energy J*/m^2 (0 K)
$Pd_{32}Cu_{32}$	3.85	1.37
$Pd_{28}Cu_{32}(T5)_4$	4.81	1.37
$Pd_{32}Cu_{28}(G5)_4$	-2.24	1.45
$Pd_{32}Cu_{28}(G6)_4$	-4.59	1.47
$Pd_{32}Cu_{28}(J6)_4$	6.67	1.47
$Pd_{32}Cu_{28}(G4)_4$	0.55	1.45

VASP: PAW GGA PW hard potentials

Surface Energy=$(E_{slab}$ (0 K) – E_{bulk} (0 K))/(2*surface area)

$Pd_{32}Cu_{28}TM_4$
8 layer (110) slab with substituent revealed at surface
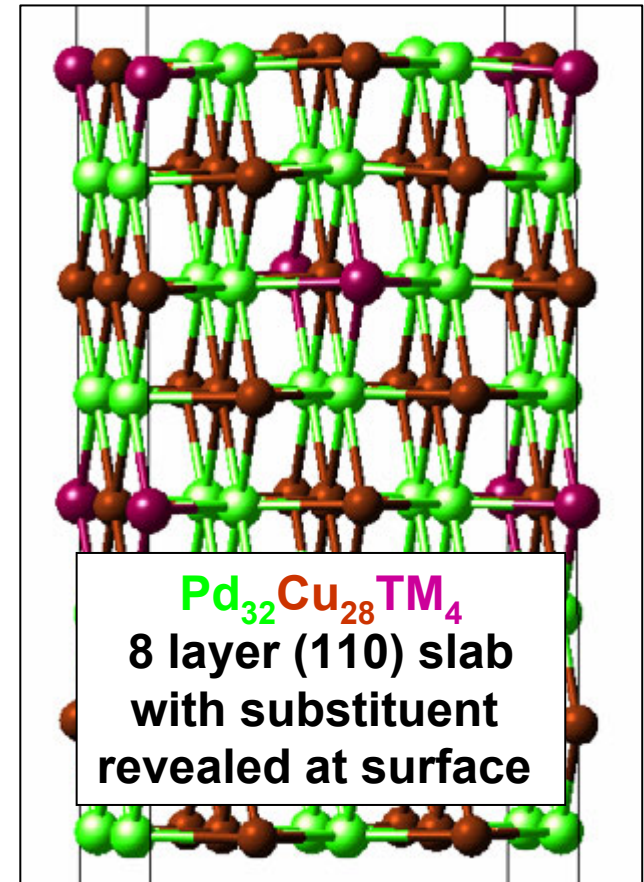
Most TM substituents increase surface energy, indicating a negative tendency for substituent surface segregation.

Down-selection of TM Alloying Agent for $Pd_{0.5}Cu_{0.5}$ B2

Modeled Property	TM Substituent – **G5**	TM Substituent – **G6**	TM Substituent – **J6**
Alloy $\Delta H_{substitution}$	Very spontaneous	Very spontaneous	Slightly endothermic
Alloy ΔVolume	Significant	Significant	Somewhat significant
Alloy Surface Energy	High	High	Very High
TM Oxidation	Very High	Very High	High, may be reducible
TM Sulfidation	Very low	Very low	Low
Pd-TM Intermetallic	Yes	Yes	Possible
TM-H Hydrides	Yes	Yes	No
TM Cost	Low	10X higher	Low

Virtual down-selection criteria included substitution favorability, impact on structure, substituent reactivity, competing substituent phases, and cost.

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VASP Calculations Show That Properly Doped TiO$_2$ System May Have Advantages Over Non-doped TiO$_2$ For H$_2$S Operation

High steam to H$_2$S ratio may be necessary to prevent oxide sulfidation

System	H$_2$S-Pt eV	OC-Pt eV	OC-Oxide eV	H$_2$S- Oxide eV
Pt/TiO$_2$ Anatase (101)	-0.76	-1.67		
Pt/Ti$_{(1-x)}$J6$_x$O$_2$	**-0.40**	**-0.97**		
PtCe$_{0.5}$Zr$_{0.42}$J6$_{0.08}$O$_2$	-2.04	-1.74		
TiO$_2$ Anatase (101)			-0.32	-1.93
Ti$_{(1-x)}$J6$_x$O$_2$ Surface			-0.85	-2.17
Ce$_{0.5}$Zr$_{0.42}$J6$_{0.08}$O$_2$ Surface			-0.63	-2.14

- H$_2$O vs oxide surface and CO, H$_2$O and H$_2$S versus subsurface dopants underway

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WGS Catalyst Development - Oxide Characterization

4 of 5 Catalysts satisfy requirements for desired state

Surface Area / Pore Volume Information

Target Material	Surface Area (m^2/g)	Pore Volume (cm3/g)	Pore Diameter (Å)
1. $Ce_{0.53}Zr_{0.38}J6_{0.1}O_2$	216	0.28	53
2. TiO_2	238	0.53	91
3. $Ti_{0.8}Ce_{0.2}O_2$	290	0.64	88
4. $Ce_{0.333}Zr_{0.333}E4_{0.333}O_2$	246	0.39	63
5. $Ce_{0.3}Zr_{0.3}E4_{0.3}J6_{0.1}O_2$	244	0.44	72

Structural Information

| Target Material	Desired State	Phase (by XRD)	Crystal Size
1. $Ce_{0.53}Zr_{0.38}J6_{0.1}O_2$	Cubic CeO_2, no separate J6Ox phase	64% cub /36% tetr, no J6Ox	2.5 nm
2. TiO_2	Anatase (100%)	85% anatase, 15% brookite	6.2 / 1.7 nm
3. $Ti_{0.8}Ce_{0.2}O_2$	Single doped phase	Multi-Phase Separation (TiO_2, CeO_2, Ce_2TiO_5, Ce_2TiO_7)	
4. $Ce_{0.333}Zr_{0.333}E4_{0.333}O_2$	Cubic $CeZrO_2$, no separate E4Ox phase	70% cub/ 21% tetr, no anatase	2.4 nm
5. $Ce_{0.3}Zr_{0.3}E4_{0.3}J6_{0.1}O_2$	Cubic $CeZrO_2$, no separate E4Ox or J6Ox phase	100% cubic	2.0 nm

WGS Catalyst Development - Platinum / Rhenium Loading

Results

CATALYST	COMPOSITION (by synthesis)	COMPOSITION (by ICP analysis)	DESIRED Pt wt%	Achieved Pt wt%	Re wt% loaded
ST WGS-01	$Ce_{0.53}Zr_{0.38}J6_{0.1}O_2$	$Ce_{0.54}Zr_{0.35}J6_{0.11}O_2$	2.0	2.09	1.045
ST WGS-02	TiO_2	TiO_2	2.0	0.60	0.30
ST WGS-05	$Ti_{0.8}Ce_{0.2}O_2$	$Ti_{0.88}Ce_{0.12}O_2$	2.0	2.11	1.055
ST WGS-06	$Ce_{0.333}Zr_{0.333}E4_{0.333}O_2$	$Ce_{0.36}Zr_{0.32}E4_{0.33}O_2$	2.0	1.97	0.985
ST WGS-07	$Ce_{0.3}Zr_{0.3}E4_{0.3}J6_{0.1}O_2$	$Ce_{0.32}Zr_{0.28}E4_{0.31}J6_{0.09}O_2$	2.0	1.74	0.87

Two Catalyst Families Down Selected for Next Phase

Subject to H₂S Aging Study Currently Underway

- Ceria Based: $Ce_{0.50}Zr_{0.40}J6_{0.10}Ox$ & $Ce_{0.33}Zr_{0.33}E4_{0.33}O_x$
- Titania Based: TiO_2 ($Ti_{0.9}J6_{0.1}O_2$ and $Ti_{(1-x)}Dp_xO_2$)

7.5% CO, 31.6% H_2O, 7.9% CO_2, 6.4% H_2, 46.6% N_2, 300,000 hr^{-1}, 1.05 Atm
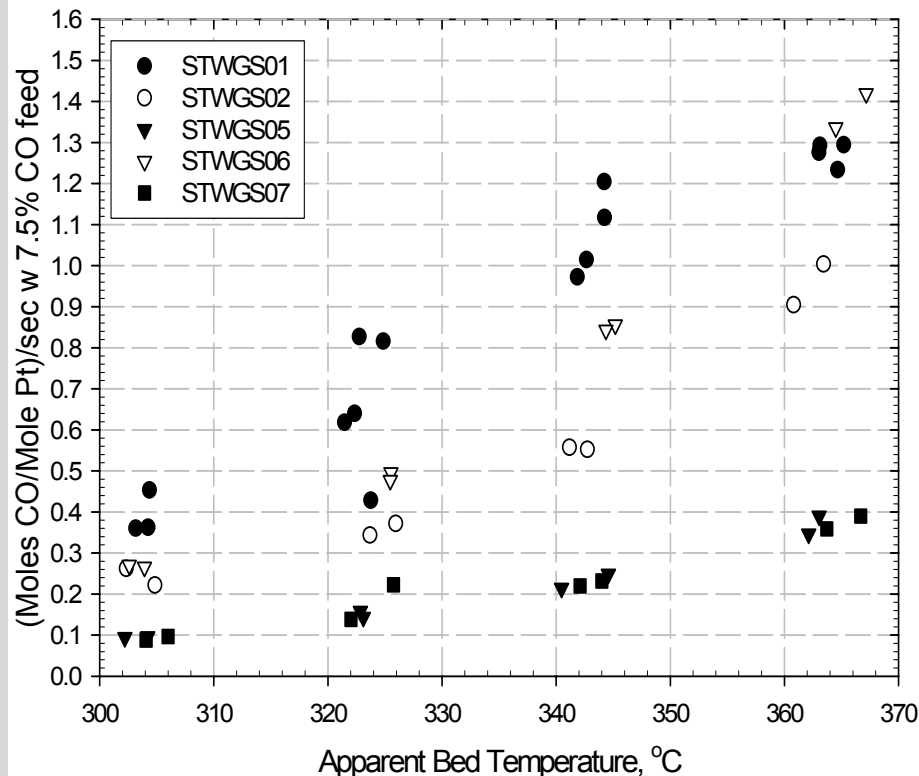
14.0% CO, 31.0% H_2O, 14.9% CO_2, 12.0% H_2, 28.1% N_2, 300,000 hr^{-1}, 1.05 Atm
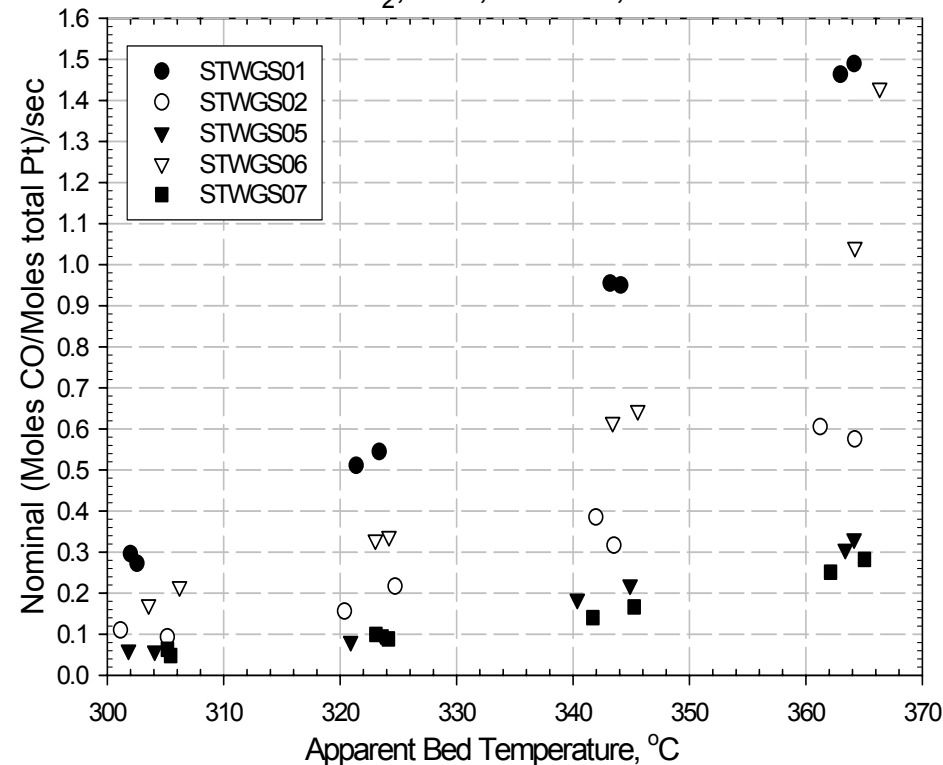
Early Kinetics Suggest Key Mechanistic Differences

Multiple site or Gorte type mechanism evident in Pt-Re/$Ce_{0.53}Zr_{0.38}J6_{0.1}O_2$ while Pt-Re/ TiO_2 seems dominated by metal site mechanism.

Catalyst	Composition (by synthesis)	n_{CO}	n_{H2O}	n_{CO2}	n_{H2}	E / kJ.mol^{-1}
STWGS-01	**$Ce_{0.53}Zr_{0.38}J6_{0.1}O_2$**	**0.32**	**1.0**	**0.85**	**0.87**	**51.4±0.1**
STWGS-02	TiO_2	-0.22	0.85	0.57	0.28	75.5±6.8
STWGS-05	$Ti_{0.8}Ce_{0.2}O_2$	1.0	1.0	0.70	0.81	81.5±8.4
STWGS-06	$Ce_{0.333}Zr_{0.333}E4_{0.333}O_2$	0.70	1.0	0.73	1.0	72.4±9.6
STWGS-07	$Ce_{0.3}Zr_{0.3}E4_{0.3}J6_{0.1}O_2$	1.0	1.0	0.72	0.78	70.2±7.0

Parity Plot for STWGS01
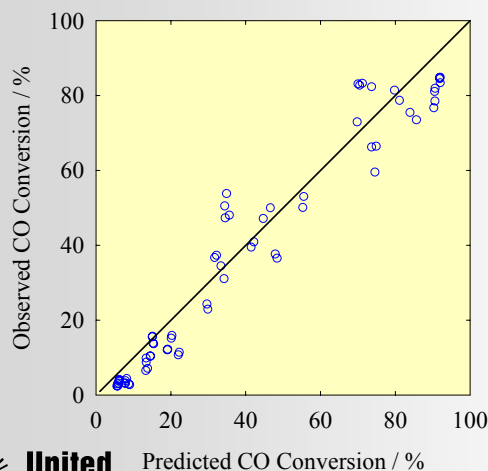
Residuals Plot for STWGS01
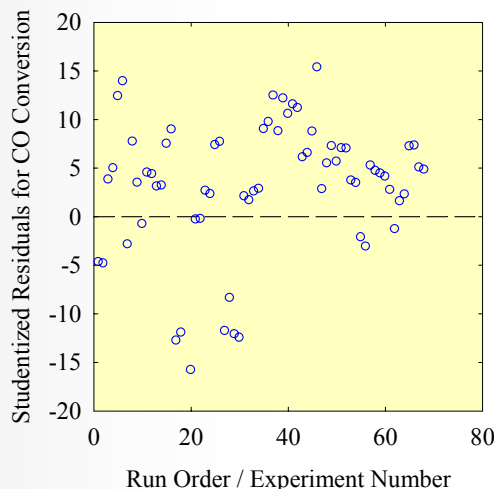
$$r_{\text{WGS}} = k P_{\text{CO}}^{n_{\text{CO}}} P_{\text{H}_2\text{O}}^{n_{\text{H}_2\text{O}}} P_{\text{CO}_2}^{n_{\text{CO}_2}} P_{\text{H}_2}^{n_{\text{H}_2}} \times (1 - \beta)$$

$$\beta = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}} K_{eq}}$$

• Additional kinetics, sulfur and aging experiments planned

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Future Work

- (Apr-Jun '06) Complete selection of optimum ternary compositions from solid-state, thermodynamic, and H_2 diffusivity parameter predictions made for two ordered Pd-Cu compositions substituted with varying levels of the two TM BCC stabilizing candidates.

- (Jul-Sep '06) Select a final PdCuTM composition through virtual refinement of phase stability, hydrogen permeability, and resistance to sulfide formation. Complete evaluation of the first set of five WGS catalyst candidates for performance in the presence of 0.004 atm H_2S. Identify through a combination of modeling and kinetic analysis and the prepare the next set of 5 WGS Catalyst candidates

- (Oct-Dec '06) Determine sulfur free kinetics of 2nd set of 5 catalysts.

- (Jan-Mar '07) Complete evaluation of 2nd set of 5 catalysts and complete catalyst atomistic modeling and synthesize final set of catalysts.

- (Apr-Jun '07) Complete evaluation of final set of catalysts and deliver final report.

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Advanced Membrane Reactor Water Gas Shift Summary

Relevance Lower cost high purity H_2 production from precleaned coal gas: Eliminates need for: 1) complete sulfur scrubbing, 2) separate H_2 extraction/purification train and retentate gas is >90% CO_2 on a dry basis.

Approach

- Atomistic and thermodynamic modeling to design high stability BCC Pd-Cu based trimetallic alloy with commercial relevant permeance.
- Design synthesize and test catalyst tailored to needs of AMR

Accomplishments

- Two "stabilized" BCC alloys $Pd_{0.5}Cu_{(0.5-x)}G5_x$ and $Pd_{0.5}Cu_{(0.5-x)}J6_x$ down selected.
- Dopants that could potentially reduce H_2S impact on Pt based WGS activity identified.

Issues

- Mechanical difficulties have delayed high pressure and sulfur testing, but identification of next set of 5 catalysts still expected in July

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Responses to Previous Year Reviewers' Comments

- Project underway less than 1 year, no reviewers' comments form last year

Publications and Presentations

- S. M. Opalka, T. H. Vanderspurt, S. C. Emerson, D. A. Mosher, Y. She, X. Tang, and D. L. Anton, "Theoretical Contributions Towards the Development of Storage Media and Related Materials for Hydrogen Processing", invited presentation, 2006 TMS Annual Meeting, San Antonio, Texas, March 13-16, 2006.

- S. M. Opalka, Y. She, W. Huang, D. Wang, T. B. Flanagan, S. C. Emerson, and T. H. Vanderspurt, "Hydrogen interactions with the ordered BCC PdCu alloy," invited presentation to be given at MH2006 International Symposium on Metal-Hydrogen Systems, Lahaina, HI, October 1-6, 2006.

BACKUP

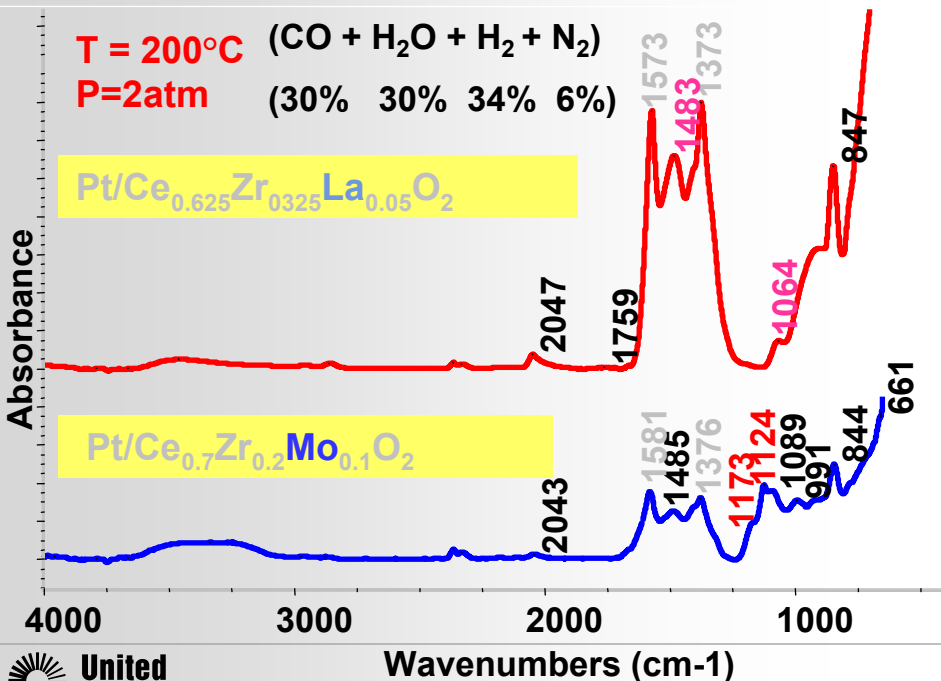- Slides reflect either work from past efforts or details from present effort

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VASP Modeling Insights Led To Better Catalysts
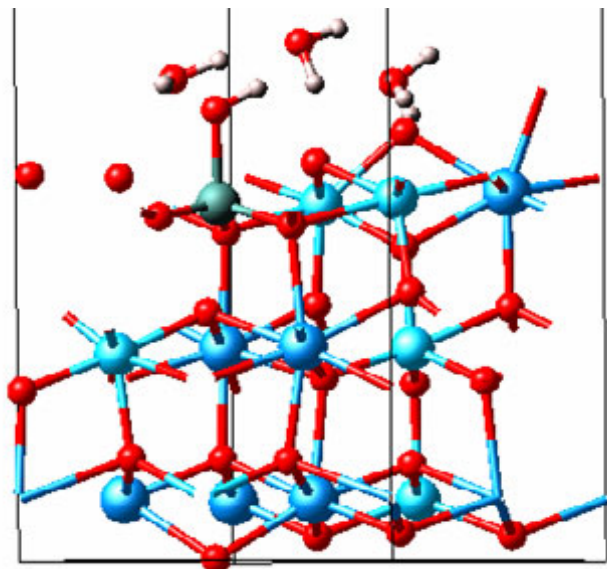
Calculated Coupled Enthalpies

$$Dp_xCe_{12-(x+y)}Zr_yO_{24} \rightarrow Dp_xCe_{12-(x+y)}Zr_yO_{23} + O$$
$$H_2O \rightarrow H_2 + O \quad CO + O \rightarrow CO_2$$
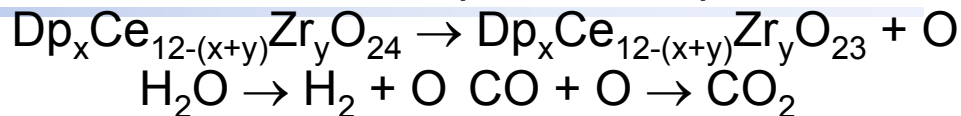
Oxide Slab	kJ/Mole	kJ/Mole
$Ce_{12}O_{24}$	+154.5	-222.4
$Ce_7Zr_5O_{24}$	+154.5	-222.1
$TaCe_6Zr_5O_{24}$	-77.2	9.6
$MoCe_6Zr_5O_{24}$	-48.3	-19.3

T = 200°C   (CO + H$_2$O + H$_2$ + N$_2$)
P = 2atm   (30%   30%   34%   6%)

Pt/Ce$_{0.625}$Zr$_{0.0325}$La$_{0.05}$O$_2$

Pt/Ce$_{0.7}$Zr$_{0.2}$Mo$_{0.1}$O$_2$

1573 1483 1373 847
2047 1759 1064

1581 1485 1376 1173 1124 1089 991 844 661
2043

Absorbance

Wavenumbers (cm-1) 4000 3000 2000 1000

Pt/Mo Doped CeZrOx

Pt/CeZrOx

(MircoMoles CO/Sec)/Gram Catalyst

Symbol	Description
●	Pt /Mo$_{0.1}$Ce$_{0.7}$Zr$_{0.2}$ 173 m^2/g
○	Pt/Mo$_{0.1}$Ce$_{0.7}$Zr$_{0.2}$ 191m^2/g
▼	Pt/ Ce$_{0.65}$Zr$_{0.35}$ 187 m^2/g Run 2
▽	Pt/ Ce$_{0.65}$Zr$_{0.35}$ 187 m^2/g Run 1

Temp C, Initial Down Ramp 4.9% CO, 10.5%CO$_2$, 33%H$_2$O, 30.3%H$_2$

Higher Activity Catalyst w Similar Pt & SA

Doping Has Increased Catalyst Thermal Robustness

- $Ce_{0.52}E6_{0.38}J6_{0.1}O_2$ retains estimated 65% of 100 hr lined out activity after 40,000 hr at 420°C w/o S
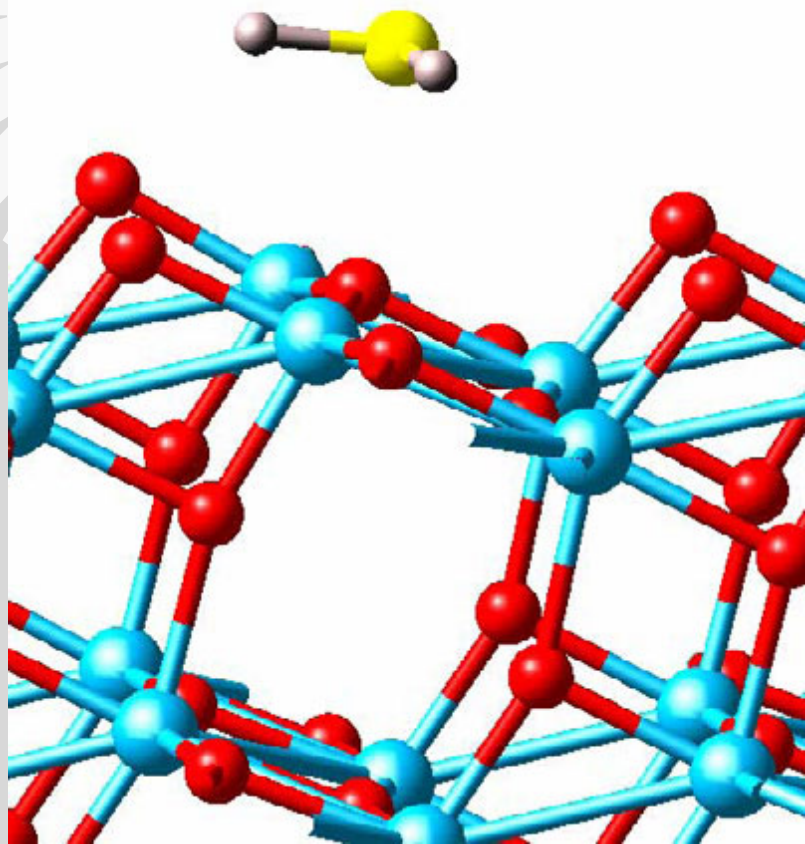
- $Ce_{0.58}Zr_{0.42}O_2$ catalyst retains estimated 54% of 100 hr lined out activity after 40,000 hr at 369°C w/o S

- $Ce_{0.5}Zr_{0.41}J6_{0.09}O_2$ retains estimated 20% of 100 hr lined out activity after 40,000 hr at 400°C with 2 ppm S
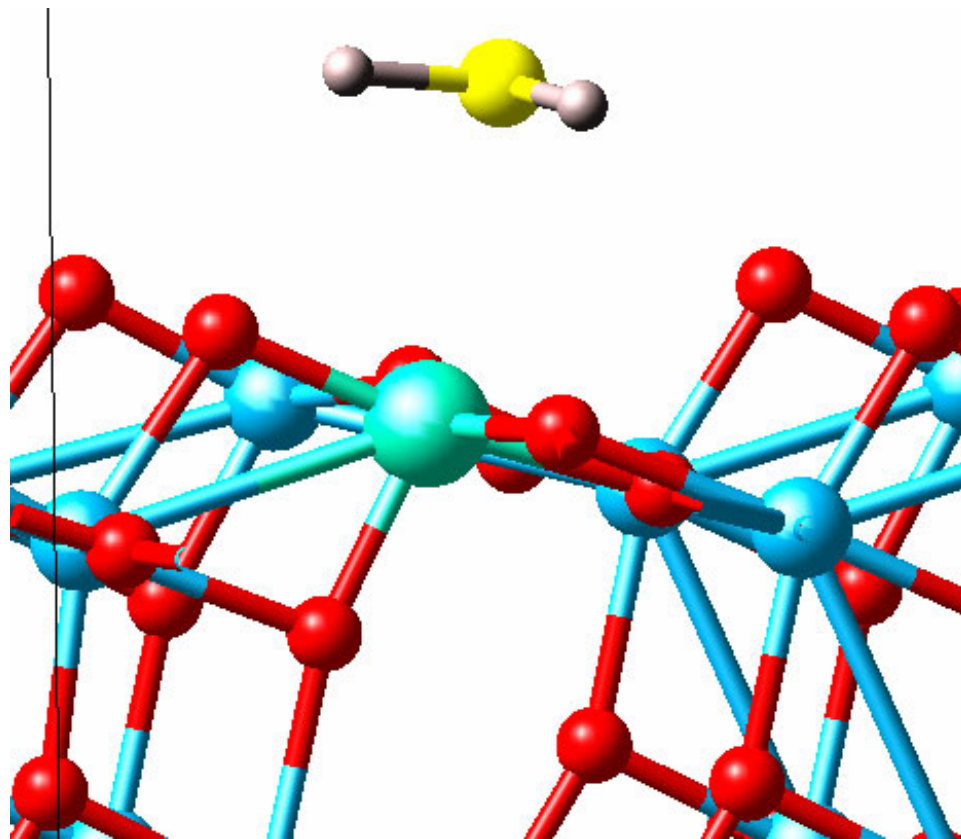
- Oxide prepared on a multi-kg pilot plant scale had a surface area/skeletal oxide volume of ~970 $m^2/cm3$

Left plot legend:
- **369°C** Pt-Re/$Ce_{0.58}Zr_{0.42}O_2$ 1363 m^2/cm^3
- **420°C** Pt-Re/$Ce_{0.52}E6_{0.38}J6_{0.1}O_2$ 1210 m^2/cm^3
- 7.5% CO, 27.6% H_2O, 5.6% CO_2, 28.9% H_2 Bal. N_2

X-axis: Log_{10}(Hours at Temperature)
Y-axis: (Moles CO/Sec)/Moles Pt

Pt-Re/$Ce_{0.5}Zr_{0.41}J6_{0.09}O_2$ Pilot Plant Scale Catalyst 400 °C, 900,000 hr^{-1} SV 2 ppm H_2S

10% CO, 29.7% H_2O, 5.7% CO_2, 16.5% H_2, Bal. N_2

X-axis: Hours on Reformate
Y-axis: Rate(MolesCO/Mole Pt)/Sec

26
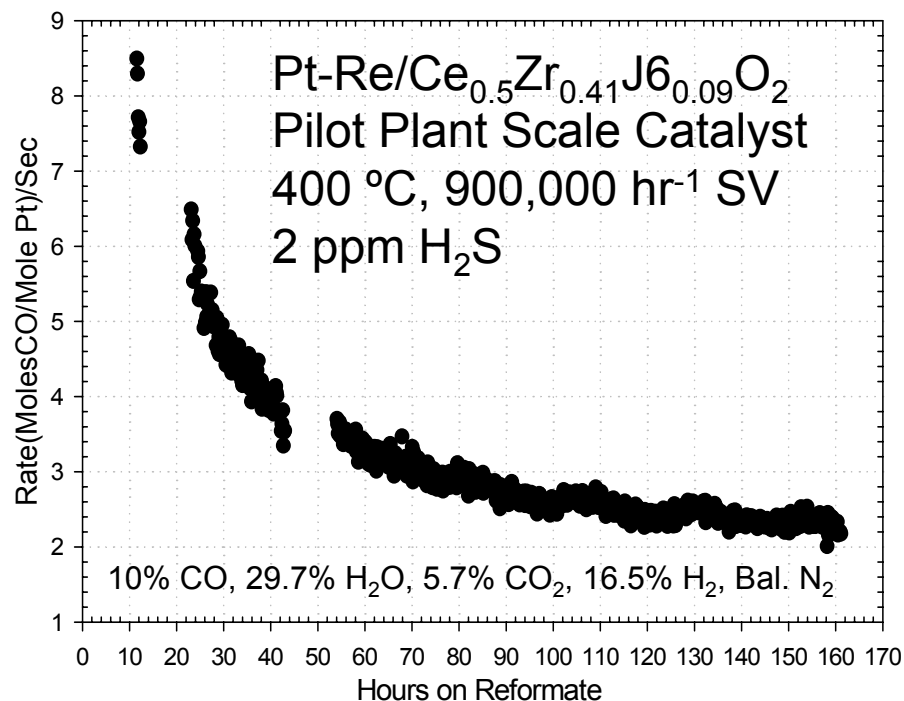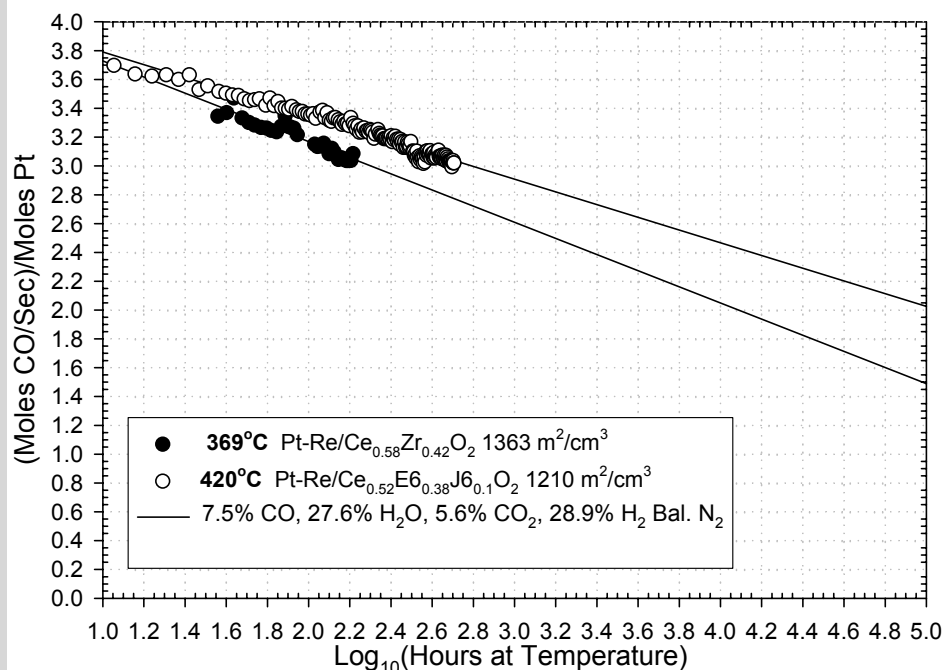
H$_2$S Adsorption

H$_2$S/TiO$_2$ Anatase(101)
Binding Energy: -1.93 eV/H$_2$S

H$_2$S/J6-Doped TiO$_2$ Anatase(101)
Binding Energy: -2.17 eV/H$_2$S

Ti J6 O H S
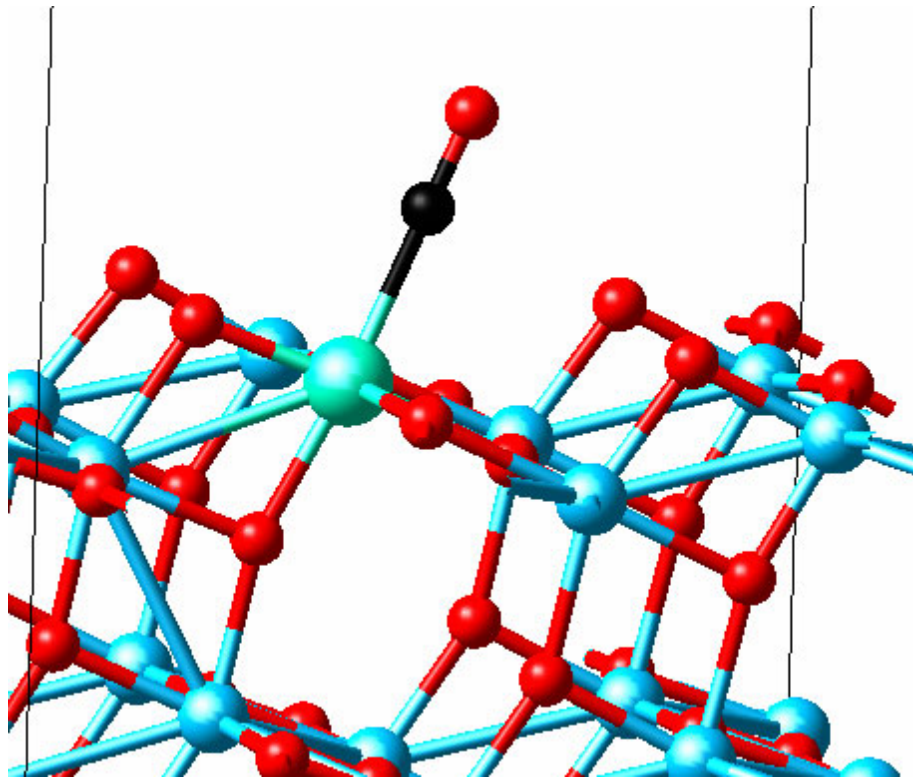
H$_2$S Adsorption
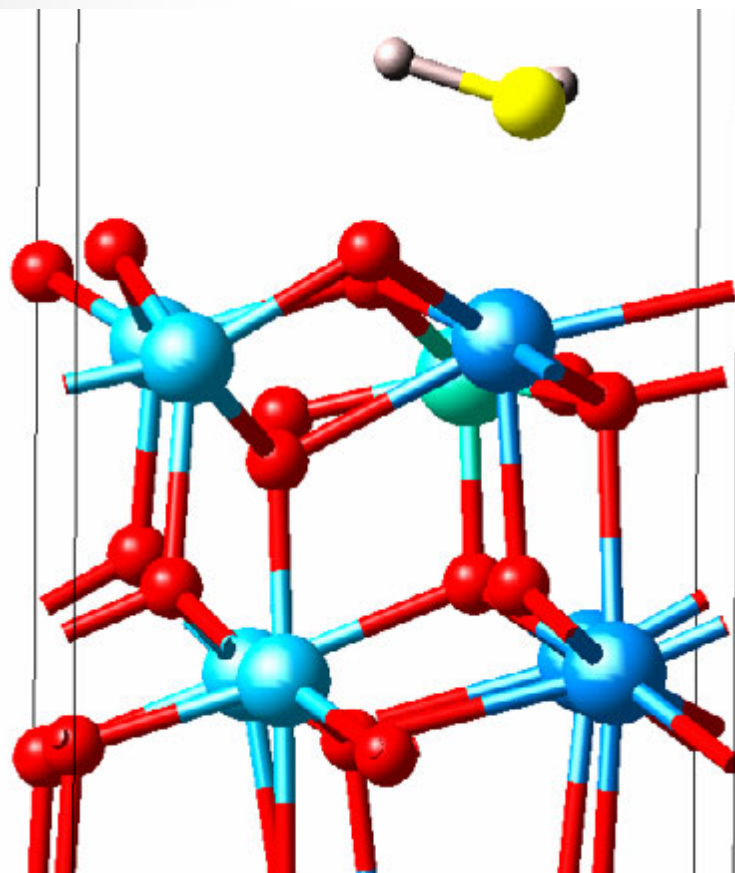
H$_2$S/Ce$_{0.5}$Zr$_{0.42}$J6$_{0.08}$O$_x$ (111)
Binding Energy: -2.14 eV/H$_2$S

Ce Zr J6 O S H

CO Adsorption
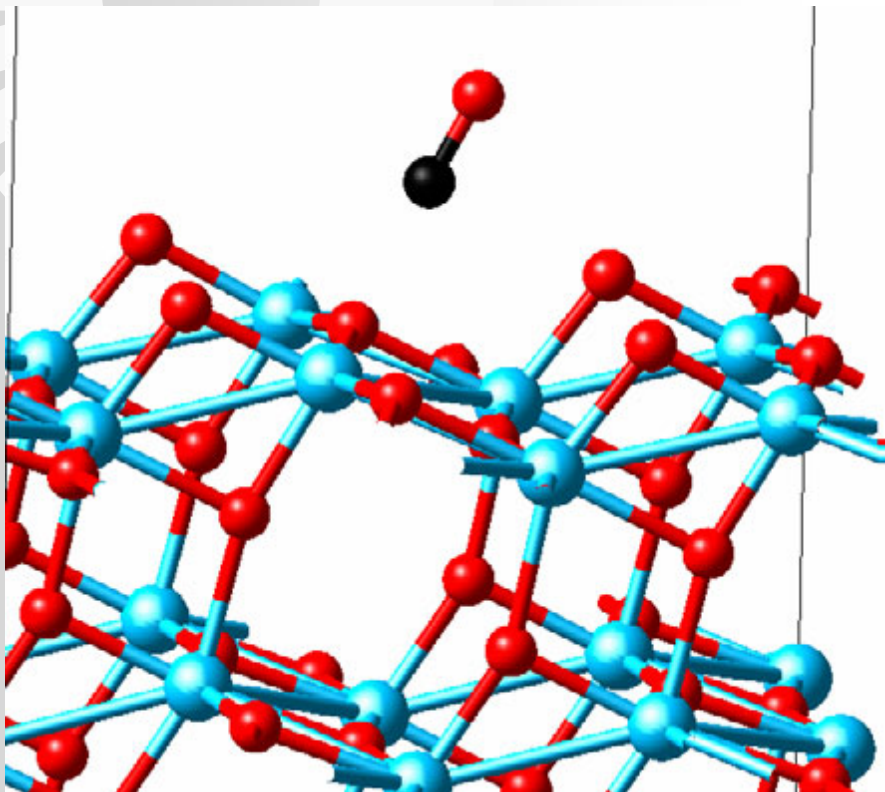
CO/TiO$_2$ Anatase(101)
Binding Energy: -0.32 eV/CO

CO/J6-Doped TiO$_2$ Anatase(101)
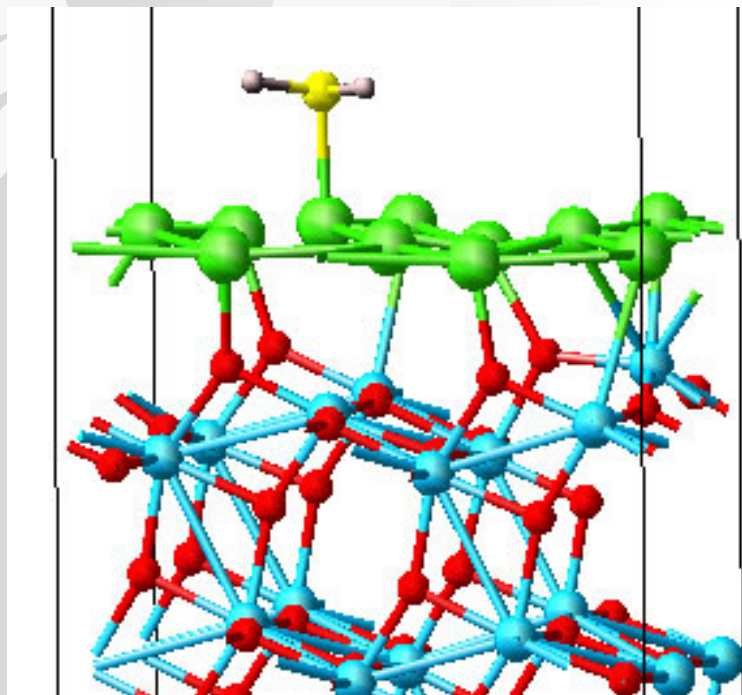Binding Energy: -0.85 eV/CO

Ti J6 C O

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Research Center
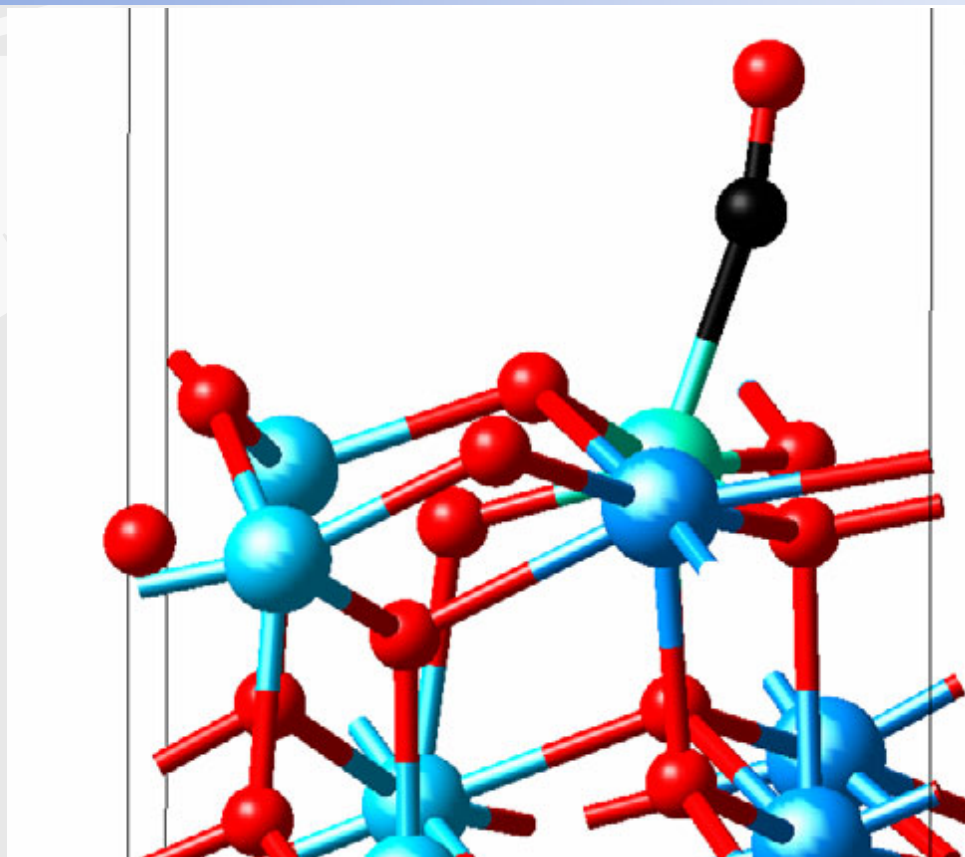
CO Adsorption

CO/Ce$_{0.5}$Zr$_{0.42}$J6$_{0.08}$O$_x$(111)
Binding Energy: -0.63 eV/CO

Ce Zr J6 O C

H$_2$S Adsorption (Pt ML)

H$_2$S/Pt$_{1ML}$/TiO$_2$Anatase(101)

Binding Energy:-0.76 eV/H$_2$S
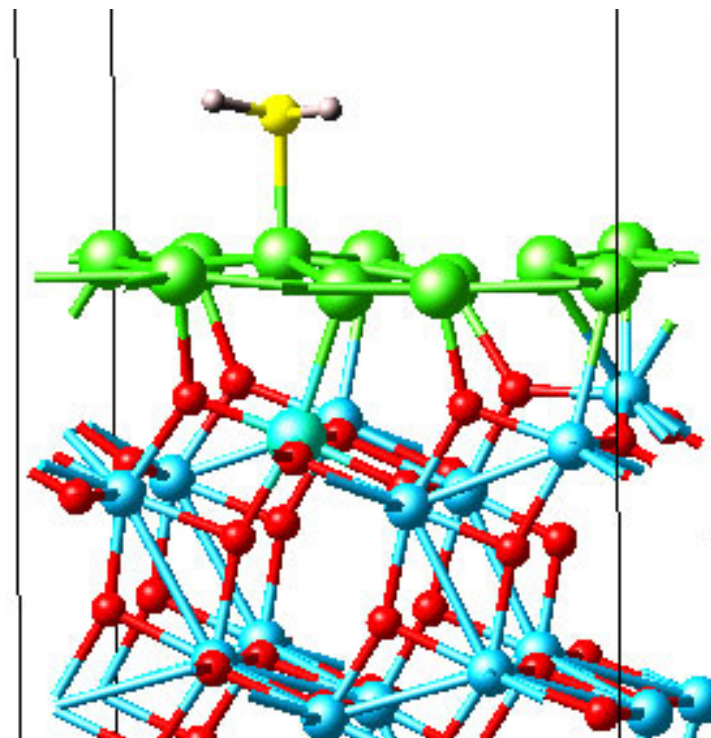
H$_2$S/Pt$_{1ML}$/J6-Doped TiO$_2$Anatase(101)

Binding Energy:-0.40 eV/H$_2$S

Pt O J6 Ti S H

United Technologies   Research Center

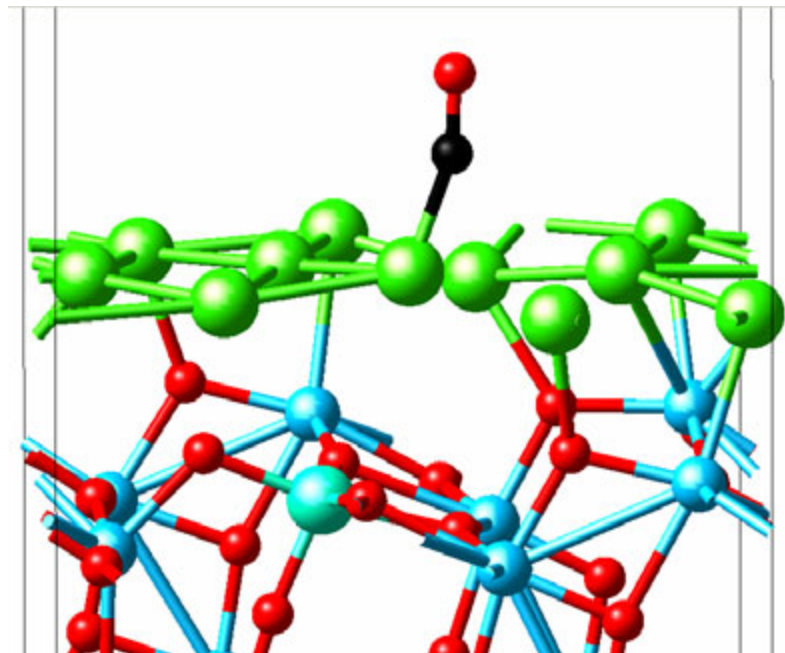# H$_2$S Adsorption (Pt ML)
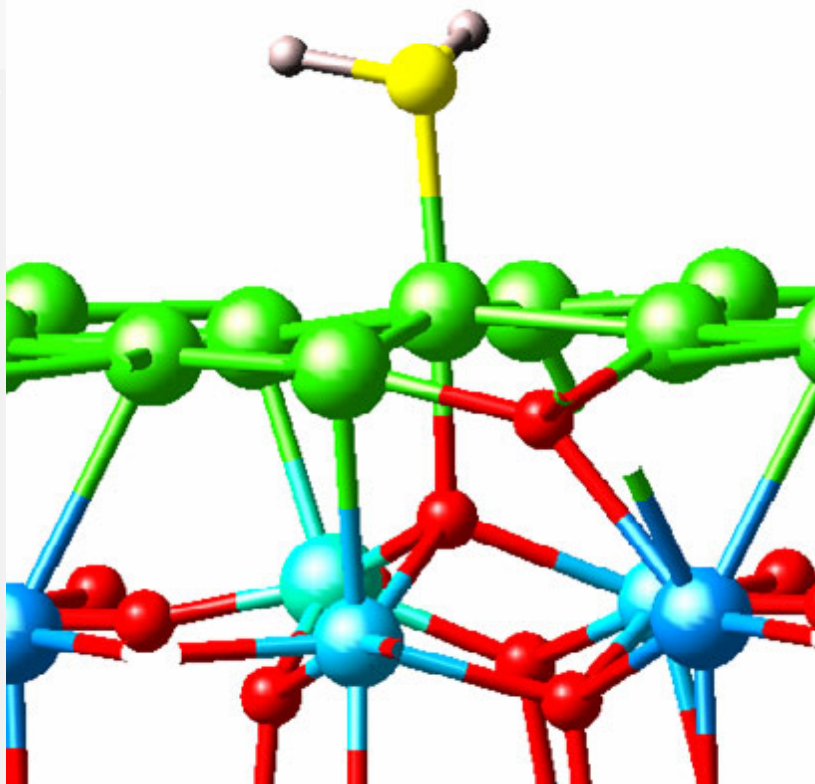
H$_2$S/Pt$_{1ML}$/ Ce$_{0.5}$Zr$_{0.42}$J6$_{0.08}$(111)

Binding Energy: -2.04 eV/H$_2$S

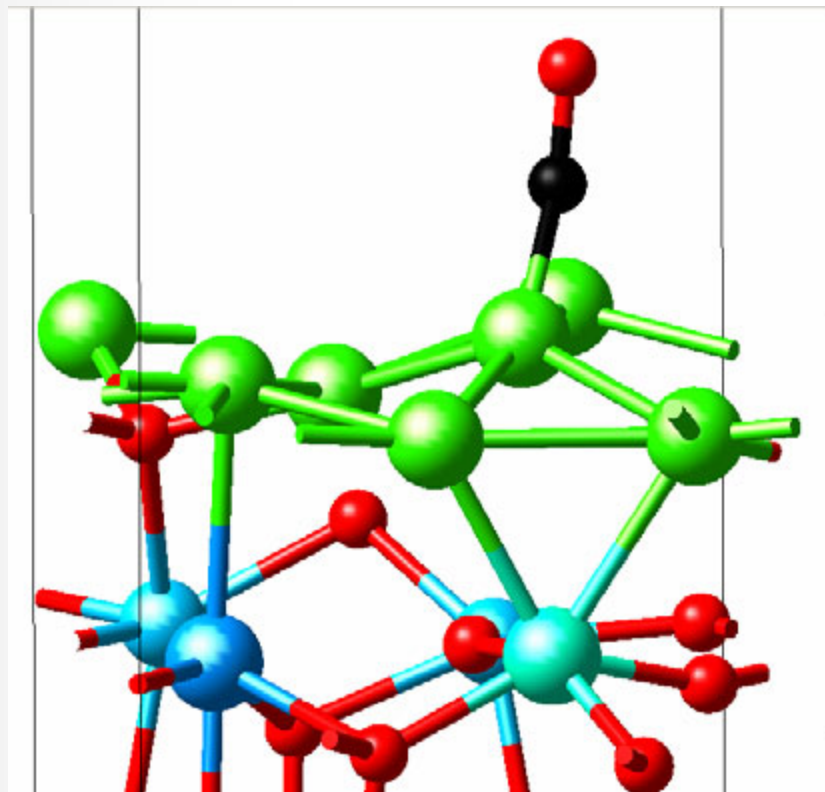Pt Ce Zr J6 O S H

CO Adsorption (Pt ML)
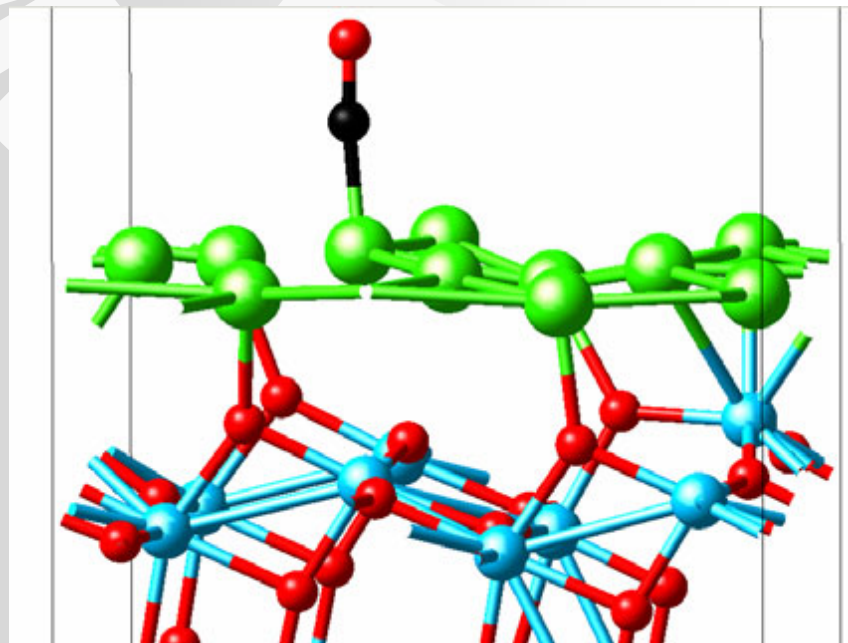
CO/Pt$_{1ML}$/TiO$_2$ Anatase(101)
Binding Energy: -1.67 eV/CO

CO/Pt$_{1ML}$/J6-Doped TiO$_2$ Anatase(101)
Binding Energy: -0.97 eV/CO

Pt Ti J6 C O
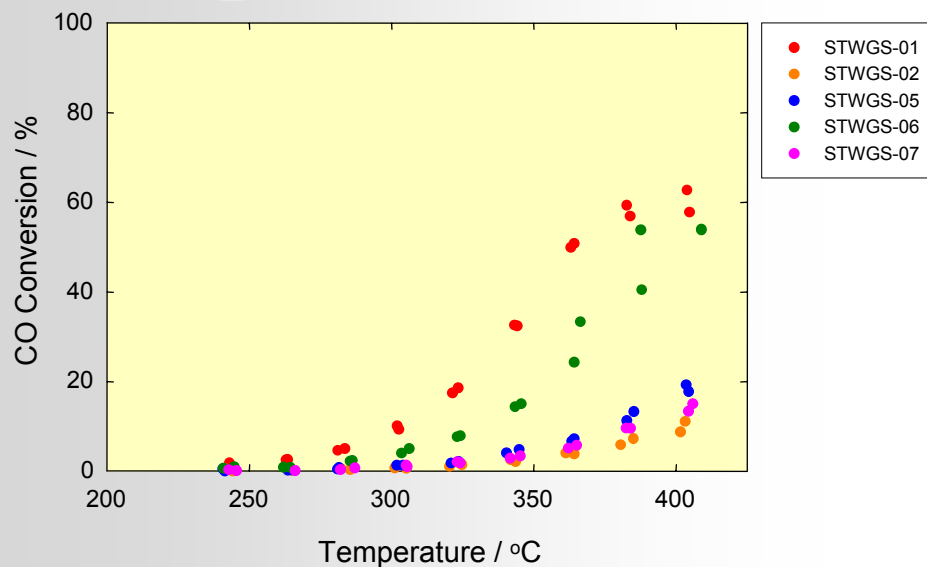
CO Adsorption (Pt ML)

$CO/Pt_{1ML}/Ce_{0.5}Zr_{0.42}J6_{0.08}O_x$
Binding Energy: -1.74 eV/CO

Pt Ce Zr J6 O C

Sulfur-free CO Conversion of WGS catalysts

Feed Conditions: 14% CO, 31% H_2O, 14.9% CO_2, 12% H_2

Feed Conditions: 7.5% CO, 31.6% H_2O, 7.9% CO_2, 6.4% H_2